STUDIES IN THE SEPARATION OF GASES BY THERMAL DIFFUSION

BY

CHARLES ELMER HOLLEY, Jr.

A.B., University of Illinois, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

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THE SEPARATION OF GASES BY THERMAL DIFFUSION

INTRODUCTION

Thermal diffusion became of considerable interest recently with the announcement of the separation of the chlorine isotopes[1]. Although the phenomenon had been predicted from theoretical considerations [2,3] and verified experimentally[4], the process had to be made cumulative before it was of practical use in the separation of gases. All workers up to the present time have been interested chiefly in separating gaeses in which the species of molecules composing the gas differ in mass. During the course of a preliminary experiment in the laboratory here some separation of a carbon dioxide—propane mixture was obtained. This led to an investigation of the separation obtainable in other pairs of gases of the same molecular weight.

EXPERIMENTAL

The thermal diffusion column was constructed of brass tubing 9 feet in length. The inner, hot tube was 0.4 inch in outer diameter while the outer, cold tube was 1 inch in diameter. They were threaded at the top so that they screwed together and the inner tube was centered by means of centering pins at the bottom. A water jacket fitted around the cold tube while the hot tube was heated by a coil of No. 22 Chromel A wire mounted on alundum thermocouple tubing and enclosed in a glass sheath. A thermocouple was fastened to the hot tube with its junction about three feet from the top. The temperatures of the hot and cold tubes were 235°C. and 20°C. respectively.

DISCUSSION OF RESULTS

The results are given in the accompanying Table I.

TABLE I

Gas Mixture	Original Composition	Final Composition Top	Bottom	Difference top-bottom
CO_2—C_3H_8	34.4%CO_2	36.5	33.6	2.9
	56.6	55.9	52.9	3.0
	69.1	70.2	67.9	2.3
CO_2—N_2O	36.1%CO_2	37.1	35.2	1.9
	42.5	43.3	41.4	1.9
	54.5	55.0	53.4	1.6
	70.1	70.4	69.0	1.4
N_2O—C_3H_8	33.9%N_2O	34.9	33.7	1.2
	48.0	48.2	46.7	1.5
	66.5	67.4	65.5	1.9
CO—N_2	26.8%CO	26.7	26.8	—0.1
	38.0	37.6	37.9	—0.3
CO—C_2H_4	33.8%CO	35.5	29.7	5.8
	46.7	48.8	41.4	7.4
	58.8	61.2	55.1	6.1
	73.4	77.2	72.8	4.4
N_2—C_2H_4	34.8%N_2	38.2	31.6	6.6
	48.3	53.0	45.1	7.9
	69.3	72.8	66.1	6.7

From these results we may draw some qualitative conclusions as to the relative sizes of the molecules. The theory of thermal diffusion shows that if the molecules are of the same weight and if they repel each other as centers of force according to a power greater than 5 of the distance between them, then the larger molecules will diffuse towards the colder

end of the temperature gradient. Assuming then that the index of repulsive force for each pair given in the table is greater than 5, we can say that the carbon dioxide molecule is smaller than the nitrous oxide molecule which in turn is smaller than the propane molecule. Also, the nitrogen and carbon monoxide molecules are of approximately the same size and both are smaller than the ethylene molecule. These conclusions are in agreement with the results of viscosity measurements.

If we denote the coefficient of thermal diffusion by D_T and of ordinary diffusion by D_{12} we can define the quantity α given by

$$\alpha = \frac{-1}{n_{10}n_{20}} \quad \frac{D_T}{D_{12}}$$

where n_{10} and n_{20} are the mol fractions of species 1 and 2 respectively. For the calculation of α from experimental results a knowledge of D_{12} is necessary. This information is available for the mixtures carbon dioxide—nitrous oxide, carbon monoxide—nitrogen, and carbon monoxide —ethylene. Consequently, an α experimental can be calculated for these mixtures[5] and compared with an α theoretical calculated by the use of cross-sections obtained from viscosity experiments[6]. The results of such caluculations are given in Table II.

TABLE II

Gas Mixture	Original Composition	α experimental	α theoretical
CO_2—N_2O	70.1%CO_2	.0056	.0028
	54.5	.0056	.0030
	36.1	.0069	.0032
CO—N_2	26.8%CO	.000	.0006
CO—C_2H_4	73.4%CO	.011	.046
	58.8	.013	.044
	46.7	.017	.042
	33.8	.015	.044

As can be seen from the table, there is agreement as to order of magnitude and sign.

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VITA

The author was born May 20, 1917 at Bellevue, Nebraska. He received his early education in the public schools of Illinois, California, and Idaho. He was graduated from University High School, West Los Angeles, California, in 1934. That fall he entered the University of Illinois from which he received the degree of Bachelor of Arts in August, 1937. The following year he held an assistantship in physical chemistry and in 1938-39 and 1939-40 he was a University Fellow. He is a member of Sigma Xi, Phi Kappa Phi, and Phi Lambda Upsilon.

He is a co-author of the following publications:

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